Density functional theory of dissipative systems

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(Dated: February 2, 2008)

Time-dependent density functional theory is extended to include dissipative systems evolving under a master equation, providing a Hamiltonian treatment for molecular electronics. For weak electric fields, the isothermal conductivity is shown to match the adiabatic conductivity, thereby recovering the Landauer result.

Much recent interest has focused on using single molecules as transistors for a new breed of computers[1]. The complex nature of these devices, especially the leads, suggests that their properties can be sensitive to chemical details. Thus we wish to model the transport characteristics of such devices with first-principles electronic structure methods, such as density functional theory (DFT). However, the traditional theorems of DFT do not apply to systems carrying current in finite electric fields.

Valid applications of DFT are derived from exact principles of quantum mechanics. These involve proofs of a one-to-one correspondence between densities and potentials, i.e., that a given one-electron density can only be produced by at most a single one-body potential, under a given set of restrictions. Ground-state DFT was established by Hohenberg and Kohn[2], by proving that, for interacting electrons, a given ground-state density can be produced by at most one ground-state one-body potential. We say the one-body potential, and hence all other properties, is a *functional* of the ground-state density.

Similarly, Runge and Gross (RG) showed[3] that, for interacting electrons in a given initial state, a given evolution of the one-body density can be produced by at most one *time-dependent* one-body potential, thus establishing the validity of time-dependent density functional theory (TDDFT). We usually start in a non-degenerate ground-state, so that the initial-state dependence becomes a ground-state density dependence, via Hohenberg-Kohn. A slight variation on this, proven in passing by RG, uses the one-body current density as the basic variable, called time-dependent current-density functional theory (TD-CDFT). This yields a more natural description of solids in uniform electric fields[4], including the polarization-dependence first identified by GGG[5].

On the other hand, transport problems within tradi-

tional wavefunction theory are usually handled within the Landauer formalism[6]. The molecule and contacts are placed between two infinite reservoirs at chemical potentials that differ by the voltage drop across the molecule. A standard integral over the Green's function and coupling to the reservoirs, and Fermi occupation factors, then yields the current, and thus the conductance. This can be made exact by using non-equilibrium Keldysh Green's functions[7], by imagining the system begins in the distant past with reservoirs and molecule decoupled, and the coupling turned on adiabatically to produce a steady-state current. Unfortunately, as the decoupled initial state is not the ground state of any Hamiltonian, the functional needed in TDCDFT differs in some unknown way from the usual functional[8].

The present state-of-the-art of DFT transport through single molecules is embodied by calculations such as those of Refs. [6] and [9], and many others. A self-consistent Kohn-Sham (KS) calculation is performed for a molecule trapped between two leads, and the scattering states are inserted into the (two-terminal) Landauer formula to calculate the conductance. At finite fields, the KS Green's function is significantly distorted from its zero-field value. As is well-recognized[6], use of the ground-state KS Green's function in place of the exact non-equilibrium Green's function is an unjustified approximation. In particular, when coupling between the molecule and leads is weak, the poles of this Green's function, representing resonances of the molecule, are at the KS orbital energy differences, which are *not* the true excitations of the system. Acknowledging such limitations, there have been several recent attempts to go beyond this picture[10, 11].

In the present paper, we prove a new density functional theorem that encompasses transport at finite elec-

tric fields, by including dissipation to phonons via a master equation. We derive the associated KS master equation. The new exchange-correlation (XC) potential reduces to that of TDCDFT in the limit of zero dissipation. Finally, we show how all the ingredients for a realistic calculation can be constructed.

We consider only symmetric leads. To avoid the use of reservoirs, put the entire system on a long thin ring, and thread through the center a solenoidal magnetic field. This produces a spatially uniform electric field throughout the entire system, and is equivalent to a change of gauge[12]. The system is finite, and nowhere are there two different chemical potentials. In the limit of zero bias, the Kubo response formalism can be applied, in either traditional many-body theory or DFT. Using this geometry, Kohn and Kamenev[13] showed how, by being careful with the order of limits, one can, within time-dependent Hartree theory, consider the response of the system to an AC electric field of frequency ω, and by taking $\omega \to 0$, recover the two- and four-terminal Landauer results. This procedure has been generalized to TDCDFT[14].

However, an important difficulty arises when the field is finite. For a purely electronic system, the electrons will accelerate indefinitely, and the current grow infinitely. In reality, there is dissipation due to scattering with phonons to bring the system to equilibrium. This basic phenomenon is described by the quantum Liouville equation for the density matrix of the entire system of electrons and phonons, S_{tot}:

$$\frac{dS_{tot}(t)}{dt} = -i[H_{tot}, S_{tot}(t)] \qquad (1)$$

In the case of bulk transport, Kohn and Luttinger[15] showed how, for scattering from dilute impurities in weak fields, Eq. (1) recovers the Boltzman equation, identifying the diagonal elements of the electronic density matrix with the distribution function.

In the quantum mechanics of dissipative systems, there is a well-established procedure for incorporating the effects of inelastic scattering with a reservoir into the long-time evolution of the system. In this case, the total Hamiltonian consists of the system Hamiltonian H (the electrons) and a reservoir Hamiltonian R (the phonons), coupled by K. The system Hamiltonian contains N interacting electrons. The coupling is linear in the phonon-coordinates, and involves only one-body forces on the system. Before an initial time ($t = 0$), both electrons and phonons are in thermal equilibrium at temperature T. The exact system density matrix S then satisfies

$$\frac{dS(t)}{dt} = -i[H(t), S(t)] - i\text{Tr}\,[K, S_{tot}(t)] \qquad (2)$$

where the trace is over reservoir coordinates. To derive a master equation for S alone[16], we coarse-grain over a

time scale Δt that is long compared to electronic transitions and phonon correlations, but short compared to the relaxation time, i.e., the time-scale on which the electrons are losing energy to the reservoir. This yields

$$\frac{d\bar{S}(t)}{dt} = -i[H, \bar{S}(t)] + \mathcal{C}[\bar{S}(t)] \qquad (3)$$

where $\mathcal{C}$ is a superoperator, found by applying Fermi's Golden rule to the scattering process, and determined by the coupling K and the reservoir spectral density. It is usually written in a basis of eigenstates of the time-independent (many-body) Hamiltonian, $H|A\rangle = E_A|A\rangle$. In this basis, $\mathcal{C}[\bar{S}]$ reads

$$\mathcal{C}[\bar{S}] = -\sum_{A,B} \quad \Gamma_{A \to B} \left(L_{AB} L_{BA} S + \qquad (4) \right.$$

$$\left. SL_{AB}L_{BA} - 2L_{BA}SL_{AB} \right), \qquad (5)$$

where the operators L_{BA} represent a transition from state A to state B, and the transition probabilities $\Gamma_{A \to B}$ are given by

$$\Gamma_{A \to B} = \begin{cases} \mathcal{D}(\omega_{AB})|\gamma_{AB}|^2 \left(\bar{n}(\omega_{AB}) + 1\right) & E_A > E_B \\ \mathcal{D}(\omega_{BA})|\gamma_{AB}|^2 \bar{n}(\omega_{BA}) & E_A < E_B \end{cases} \qquad (6)$$

in terms of the electron-phonon coupling elements γ_{AB}. $\mathcal{D}(\omega)$ is the density of states of phonons with frequency ω ($\omega_{AB} = E_A - E_B$), and $\bar{n}(\omega) = 1/\left(e^{\frac{\omega}{kT}} - 1\right)$ is the thermal occupation factor. The transition probabilities satisfy detailed balance

$$\exp(-E_A/k_B T)\Gamma_{A \to B} = \exp(-E_B/k_B T)\Gamma_{B \to A}, \qquad (7)$$

so that the steady-state solution of Eq. (3) yields the thermal equilibrium density matrix of H. No matter what the initial density matrix, the steady-state solution is always the same. Thus the master equation couples statistical mechanics to quantum mechanics and, by including only secular contributions, goes beyond the Schrödinger equation for the electrons to build in irreversible evolution.

As long as the coupling is weak, the rate at which the system relaxes back to equilibrium (the relaxation time) will be much longer than all other scales, and the master equation applies. While there is much discussion about the validity of the master equation, and what physics is contained within it, in what follows we take Eq. (3) as given, with all its merits and flaws, and show how to map the system to an effective single-particle system. Although the system Hamiltonian is time-independent, the time-dependence in the master equation is generated by, e.g., starting in a non-equilibrium density matrix, which evolves into the thermal equilibrium density matrix. This involves excitation and de-excitation of the electrons.

Our goal is describe a many-electron system, evolving under a master equation, by a collection of non-interacting electrons. To do this, we allow the one-body

potential of H to be time-dependent. This breaks the connection between $\mathcal{C}$ and H, since the final H might have an external electric field turned on, but the initial H not. We then construct a Runge-Gross style proof that, for fixed electron-electron interaction and superoperator $\mathcal{C}$, and for a given initial density matrix S_0, no two one-body potentials can give rise to the same time-dependent density $n(\mathbf{r}t)$. We assume that the potentials are Taylor-series expandable around $t=0$, and that some coefficient in the expansion is not uniform in space. Begin with the equation of motion for the current density:

$$
\begin{aligned}
\frac{d\langle \mathbf{j}(\mathbf{r})\rangle}{dt} &= \mathrm{Tr}\ \left(\mathbf{j}(\mathbf{r})\frac{d\bar{S}}{dt}\right) \\
&= -i\mathrm{Tr}\ \left(\mathbf{j}(\mathbf{r})[H,\bar{S}]\right) + \mathrm{Tr}\ \left(\mathbf{j}(\mathbf{r})\mathcal{C}[\bar{S}]\right) \quad (8)
\end{aligned}
$$

where $\mathbf{j}(\mathbf{r}) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i)\mathbf{p}_i + \mathbf{p}_i\delta(\mathbf{r}-\mathbf{r}_i)$ is the current-density operator. Using the fact that cyclic permutation does not alter the trace, we can write the first term on the right as $i\mathrm{Tr}\ ([H,\mathbf{j}(\mathbf{r})]S)$, which is the usual contribution from evolution under a Hamiltonian. Evaluating everything at $t=0$, and considering two systems with possibly different potentials but the same initial density matrix and coupling, we find

$$
\frac{d\Delta\langle \mathbf{j}(\mathbf{r})\rangle}{dt}\Big|_{t=0} = -n_0(\mathbf{r})\Delta\nabla v_{\mathrm{ext}}(\mathbf{r}t=0) \quad (9)
$$

just as in RG. Thus two potentials that differ at $t=0$ give rise to two different currents.

One next shows that, for two systems whose initial Hamiltonians are the same, and two operators that are identical initially, but whose time-evolution differs,

$$
\frac{d\Delta\langle A\rangle}{dt}\Big|_{t=0} = \mathrm{Tr}\ \left(\frac{\partial\Delta A}{dt}\Big|_{t=0}\bar{S}(0)\right) \quad (10)
$$

within the master equation, because both the commutator and $\mathcal{C}$ are identical in both systems at $t=0$. Applying this result to the equation of motion for the k-th derivative of the currents,

$$
\partial_0^{k+1}\Delta\mathbf{j}(\mathbf{r}t) = -n_0(\mathbf{r})\ \nabla\partial_0^k\Delta v_{\mathrm{ext}}(\mathbf{r}t) \quad , \quad (11)
$$

where $\partial_0^k = (\partial^k/\partial t^k)\big|_{t=0}$. Thus, any difference in any derivative of the potentials (other than a constant), produces two different currents. This establishes a one-to-one correspondence between densities and currents.

We could stop here, as it is the TD current DFT that is needed[14] for transport calculations. But, for generality, we also wish to establish a *density* functional theory, the final step of the RG theorem uses continuity to show that the densities must differ for two different potentials. This follows in the master equation evolution, since

$$
\frac{d\langle n(\mathbf{r})\rangle}{dt}\Big|_{t=0} = -\mathrm{Tr}\ \left(\nabla\mathbf{j}(\mathbf{r})\bar{S}(0)\right) + \mathrm{Tr}\ \left(n(\mathbf{r})\mathcal{C}[\bar{S}(0)]\right) \quad (12)
$$

and the last term is the same in both systems. The usual arguments about the vanishing of the potentials sufficiently rapidly at large distances then suffice for finite systems[17], or single-valuedness for periodic systems[4]. Breakdown of continuity in the master equation occurs because, in Eq. (12), the superoperator provides a correction to the usual statement under Hamiltonian evolution, i.e., some momentum is transferred to the reservoir. But use of Eq. (12) restores continuity, and the correction can even be written in terms of a current[18].

We have established that the potential is a functional of the time-dependent current density for a given interaction, statistics, initial density matrix, and coupling. In principle, we can apply the same argument with the interaction set to zero, to produce a set of time-dependent KS equations whose one-body potential, $v_{\mathrm{s}}[n, S_{\mathrm{s}}(0), \mathcal{C}](\mathbf{r}t)$, is defined to yield the exact $n(\mathbf{r}t)$, when evolved under the master equation. By subtracting the external potential and Hartree contribution, we find an XC potential that has the same dependencies as the KS potential, but also depends on the initial density matrix of the interacting system. Fortunately, we can subsume all dependence on the initial density matrices into the functional itself, by beginning in an equilibrium distribution for both the interacting and non-interacting systems. In that case, the Mermin functional, which is just a functional of the initial density, determines the initial density matrix.

Constructed this way, the KS system has certain pathologies. The superoperator in the many-body master equation is guaranteed to vanish only on the many-body density matrix, not on the KS density matrix. To compensate for this, the corresponding KS potential might need to evolve forever, even after the KS system has settled into a steady state[8]. Nevertheless, we can construct a practical KS scheme by constructing a KS superoperator, $\mathcal{C}_{\mathrm{s}}$. To do so, we define $v_{\mathrm{s}}(T)(\mathbf{r})$ as the KS potential in the Mermin functional at temperature T, i.e., the potential that, when thermally occupied with non-interacting electrons, reproduces the exact one-electron density at thermal equilibrium. We then apply perturbation theory for a weak interaction between non-interacting electrons in this potential and the phonons in the reservoir, yielding the analogs to Eqs. (6) above:

$$
\gamma_{i\to j} = \begin{cases} \mathcal{D}(\omega_{ij})|\gamma_{ij}|^2\left(\bar{n}(\omega_{ij})+1\right) & \epsilon_i > \epsilon_j \\ \mathcal{D}(\omega_{ji})|\gamma_{ij}|^2\bar{n}(\omega_{ji}) & \epsilon_i < \epsilon_j \end{cases} \quad (13)
$$

where ϵ_i are the eigenvalues of $-\nabla^2/2 + v_{\mathrm{s}}(T)(\mathbf{r})$. The matrix elements γ_{ij} are now evaluated for the interaction between the KS system and the bath. To find the KS master equation itself, we reduce the many-body Eq. (3) to a single particle form by tracing out all other degrees of freedom, and using a Hartree-style approximation for the two-particle correlation functions appearing in $\mathcal{C}[\bar{S}]$. In the basis of the single-particle KS orbitals, $|n\rangle$, $|m\rangle$, $|p\rangle$,

we find[19]:

$$\frac{ds_{nm}}{dt} = -i \sum_p (h_{np}s_{pm} - s_{np}h_{pm})$$
$$+ (\delta_{nm} - s_{nm}) \sum_p (\gamma_{np} + \gamma_{mp}) s_{pp} \quad (14)$$
$$- s_{nm} \sum_p (\gamma_{pn} + \gamma_{pm}) (1 - s_{pp}).$$

In this KS master equation, the steady-state equilibrium has a static potential. The approach rate, determined by γ, will not match that of the true system, but such effects are absorbed in the XC potential. The important point is that, if such a KS system exists, it is unique for the given coupling, by the theorem proven above.

Next we discuss the XC functional, which depends on the coupling to the reservoir. One could imagine performing accurate wavefunction calculations for a uniform gas on a ring, with the given coupling, to produce a local density approximation for the master equation. But we argue that the usual approximations of TDDFT (or TD-CDFT, as needed), such as the adiabatic local density approximation, are likely to suffice, because the KS master equation includes dissipation, and drives the system to the thermodynamic steady state. Thus the effect of dissipation on XC is likely to be small, and might even vanish in the limit of weak coupling to the reservoir. The important XC effects are to correct the electronic transition frequencies into the true transitions, and this is captured exactly by such an approximation.

The dissipative part of the master equation, $\mathcal{C}[\bar{S}]$ in Eqs. (3) and (5) depends on phonon frequencies ω, densities of state $\mathcal{D}(\omega)$, and coupling matrix elements γ_{nm}. All these quantities can be extracted from first-principles density-functional linear response calculations[20]. This allows for a fully consistent DFT implementation of the dissipative dynamics.

Lastly, we discuss the recovery of the Landauer result for the case of transport through a single molecule, in the limit of weak bias. This has recently[14] been derived using TDCDFT. Here we show the derivation of linear response for the more familiar DFT, and the current version is essentially the same (but more cumbersome).

For a given KS master equation, assume the density matrix has evolved into its steady state, so that

$$[H_0, \bar{S}_0] = -i\mathcal{C}_s(\bar{S}_0) \quad (15)$$

If $\mathcal{C}_s$ has been constructed to thermalize the eigenstates of H_0, both sides of this equation vanish. Now imagine perturbing the system with a weak time-dependent potential ΔV, which becomes constant after a finite time. Allow the system to relax back to its new steady state, with density matrix $\bar{S}_0 + \Delta S$. Equating equal powers in the perturbation:

$$[H_0, \Delta S] + i\eta[\bar{S}_0] \cdot \Delta S = -[\Delta V, \bar{S}_0] \quad (16)$$

where η is the first derivative of $\mathcal{C}_s$. Expanding all quantities in eigenstates of H_0 and solving, we find

$$\Delta S_{AB} = \frac{f_A V_{AB} - f_B V_{AB}}{E_A - E_B + i\eta_{AB}} \quad (17)$$

where $\bar{S}_0 = \sum |A\rangle f_A \langle A|$, i.e., f_A is the Fermi occupation factor of state A. Calculating the density change by tracing the density operator with ΔS, and recognizing that the system eigenstates are Slater determinants of orbitals, one recovers the usual density-density response function[21]. A similar derivation holds for the current-current response within TDCDFT.

To understand what this means, consider a KS master equation with weak dissipation ($\eta_{ij} << \omega_{ij}$), on an infinite ring. Turn on a small but finite electric field, and evolve the system into a steady state. This is the isothermal conductivity[15], found from the steady-state solution for the electrons coupled to the phonons. The derivation above shows that this reduces to the adiabatic conductivity as given by the Kubo response formula, which has recently been shown to recover the Landauer result (with possible XC corrections)[14].

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